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⑥ THE EFFECTS OF AN IMMISCIBLE BINDER COMPONENT ON
THE RHEOLOGICAL AND MECHANICAL PROPERTIES OF
A COMPOSITE SOLID PROPELLANT, (U)

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The Improved HAWK antiaircraft missile is powered by the M112 rocket motor. This motor operates in boost and sustain modes derived from concentric booster and sustainer composite solid propellant grains (Figure 1). The booster propellant is relatively fast burning to provide the thrust level necessary to accelerate the missile to intercept velocity, while the sustainer propellant burns slowly over a much longer time to maintain missile velocity and maneuverability during the mission. The booster grain is fully bonded to the sustainer grain which in turn is fully bonded to the steel motor case by means of an adhesive case liner.

The chamber pressure of Improved HAWK motors during firing is governed by the ratio of burning surface area to the area of the nozzle throat. The internal perforation of the booster grain is shaped to a predetermined surface area. If additional area is exposed to combustion, an overpressure condition results which can burst the motor case. Another type of aberration which can defeat the mission is that flame may reach the steel case prematurely and burn a hole through it, causing the motor to lose thrust and become unstable in flight. A condition which can produce both of these malfunctions is that in which a normally bonded propellant interface is unbonded.*

*The term "unbond" denotes a condition in which there is no bond where one was intended, whether or not the intended bond ever existed. The term "debond" denotes a condition where a bond existed but is now broken.

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The stresses which tend to debond the grains from one another or from the liner are due to temperature variations in the motor environment coupled with coefficients of thermal expansion for the propellants which are an order of magnitude greater than that of the steel case. As the motor is cooled, strains are induced in the propellant with concomitant stresses on the bond interfaces. If the stresses exceed the bond strength, a debond occurs.

Several thousand Improved HAWK motors were produced without a significant unbond problem. Then, rather abruptly, a substantial number of unbonded motors appeared in one production lot. Both booster-sustainer and sustainer-liner unbonds were found, some of which were extensive in area. Because prior production had not exhibited the problem, it was assumed that a change had occurred in either motor processing or propellant raw materials.

IDENTIFICATION OF THE ANOMALOUS MATERIAL

Tests made on propellants removed from unbonded motors showed that sustainer propellant mechanical properties were significantly different at low temperatures in comparison to prior production. However booster propellant properties were normal; this isolated the problem to the sustainer propellant. Two materials are used in the sustainer propellant which are not components of the booster propellant. One of these is a solid oxidizer (nitroguanidine) while the other is a liquid polyester, poly-neopentyl glycol azelate (NPGA), a component of the propellant binder. Preparation and testing of propellants containing various lots of these two components showed that NPGA was responsible for the inferior properties found in propellants from unbonded motors.

PROPELLANT COMPOSITION AND PROCESSING

HAWK sustainer propellant consists of solid oxidizer particles imbedded in a rubbery polyurethane binder. The polyurethane binder controls the structural properties of the propellant and serves as a fuel during propellant combustion. Three hydroxy-functional liquid polymers comprise the major constituents of the rubber precursor: (1) a difunctional polyether (B2000), (2) a trifunctional polyether (TP4040), and (3) the polyester NPGA which has been found to have an effective functionality of 1.7. Isodecyl pelargonate is added to facilitate processing and to plasticize the cured propellant. The hydroxy-functional polymers are cured by reaction with hexamethylene di-isocyanate (HDI) under catalysis by ferric acetyl acetate to form the polyurethane rubber.

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In propellant manufacture, the liquid polymers and isodecyl pelargonate are blended to form a submix. The powdered solid oxidizers are then added until a homogeneous paste of high viscosity is formed. HDI and cure catalyst are added to start the cure reaction and the propellant is poured into rocket motor cases and test specimen containers before the cure reaction increases the viscosity beyond processable limits. Cure is complete after several days at a temperature of 43°C.

CHARACTERIZATION OF NPGA

Contacts with the NPGA manufacturer revealed that recent lots of the polymer, beginning with the lot that went into unbonded motors, were produced in a new facility. However, these lots met all specification requirements for use in HAWK motors (Table 1).

Samples of old and new lots of NPGA were characterized by gel permeation chromatography (GPC) to determine whether molecular weight changes had resulted from the facilities switch. The results (Figure 2) showed that the average molecular weight of the new lot was significantly higher than that of the old lot and that the molecular weight distribution was broader in the new lot, increasing the higher molecular weight fraction. However, the low molecular weight region which contains most of the hydroxyl groups was not decreased.

The effective functionality of NPGA was determined by finding the isocyanate/hydroxyl (NCO/OH) ratios required for incipient gelation in a mixture of the binder polymers cured with HDI. The results (Table 2) showed the new lot to have a significantly lower effective functionality than the old.

The viscosities of the new and old lots of NPGA were measured at 25°C and 43°C; the ratios of viscosities at these temperatures were compared as an indication of whether there was a difference in chain branching. It was found that the ratios were not significantly different (Table 2). This indicated that the higher molecular weight of the new lot was due to chain extension rather than branching, which was in agreement with the functionality data.

EFFECTS OF NPGA DIFFERENCES ON SOLUBILITY

The new lot of NPGA produced a decidedly cloudy submix indicating incomplete solubility. Submix formulations were prepared with old and new lots of NPGA and the quantities of the insoluble fractions were determined by centrifuging samples in graduated tubes.

In the submix formulation associated with the unbonded motors, the new lot of NPGA produced an immiscible fraction equal to 39.8% of the NPGA added. The old lot of NPGA in the same formulation gave an immiscible fraction equal to 31.8% the NPGA added. Samples then were prepared to the submix formulation associated with the old lot NPGA, and the insoluble fraction of the old lot of NPGA amounted to 24% of the NPGA added. Thus it became clear that factors other than NPGA variability were affecting its solubility.

The major difference between submix formulations associated with the old and new lots of NPGA was in the relative amounts of TP4040 and B2000 in each formulation. TP4040, being trifunctional, strongly influences the binder cross-link density and thus the modulus of the propellant. Consequently, the amount of TP4040 is deliberately varied with different lots of raw materials as a means of controlling propellant modulus within specified limits.

Submix samples were prepared with TP4040 contents ranging from 2% to 6% (based on propellant weight), and the insoluble fractions of the old and new lots of NPGA were measured. The data are shown in Figure 3. Two things were immediately obvious from these data: the insoluble fraction differed for the old and new lots of NPGA at all TP4040 levels; and the insoluble fraction for both lots was a strong function of TP4040 content.

COMPOSITION OF THE INSOLUBLE FRACTION

The insoluble fraction from a submix sample made with the new lot of NPGA was analyzed on the GPC. The results are given in Table 3 with comparative data for neat NPGA. It was seen that both the number average and weight average molecular weights were much higher for the insoluble fraction than for neat NPGA. This showed that the high molecular weight fraction of NPGA was the immiscible fraction in the submix and explained why the new lot of NPGA, with a larger high molecular weight fraction (Figure 2), was less soluble than the old lot.

The compositions of the insoluble fractions were determined spectrophotometrically using samples of known composition for calibration. The results are shown in Table 4; approximately two-thirds of the insoluble fraction was found to be NPGA. Since the insoluble fraction of the submix with the new lot amounted to 39.8% of the NPGA added, and 69% of that fraction was NPGA, the amount of NPGA alone not in solution in the submix was 27.5% of the quantity added. Similar treatment of the data for the old lot showed 21.3% of the quantity added to be insoluble. These data reflect solubility of NPGA with

2% TP4040 (propellant basis) in the submix, as was the case with the new lot of NPGA. Taking into account that the submix formulation associated with the old lot of NPGA contained 3.1% TP4040, reference to Figure 3 and Table 4 shows that 16.1% of the old lot of NPGA was insoluble as actually used. Thus the comparison of solubilities in the actual production submixes reveals that 27.5% of the new lot of NPGA was insoluble while only 16.1% of the old lot was not in solution.

EFFECT OF IMMISCIBLE FRACTION ON PROPELLANT RHEOLOGY

A plausible cause for motor unbonds was that the uncured sustainer propellant might not adequately wet the booster grain and chamber liner during motor processing because of the immiscible material. Since the quantity of the insoluble fraction of the submix was a function of TP4040 content, a means was available to determine how the amount of insoluble fraction affected uncured propellant flow characteristics. Propellant mixes were made containing various amounts of TP4040. Viscosity data were taken with a viscometer capable of applying a range of shear stresses to the sample. Viscosities were measured at 43°C immediately following a fixed mixing cycle. Measurements were made at high and low shear stresses. The results are shown in Figure 4 for propellants made with the new lot of NPGA.

The data showed that insoluble fractions amounting to less than approximately 20% of the NPGA produced low propellant viscosities at both levels of shear stress. The ratio of viscosities at the two shear levels was small at this solubility, indicating near-Newtonian flow behavior. As the insoluble fraction was increased, the viscosity at infinite shear increased only slightly, but the low shear viscosity increased rapidly. The ratio of viscosities increased correspondingly, indicating an increasing degree of thixotropy in the flow behavior. The ratio of viscosities, which was 1.6 at an insoluble fraction of 18%, was 9.6 at a 40% insoluble fraction. Taking appropriate data from Figures 3 and 4, a viscosity ratio of 1.7 is predicted for propellant with old NPGA and 9.6 for propellant with the new lot. Control data from production mixes agreed reasonably well with these findings, showing a viscosity ratio of 1.7 for propellants made with the old lot of NPGA, and 4.5 for propellant with the new lot.

EFFECT OF THE IMMISCIBLE FRACTION ON PROPELLANT MECHANICAL PROPERTIES

Certain mechanical properties of the propellants are specified control points for Improved HAWK motor production. One of these is the initial modulus (E_0) at 25°C, which should be in the range from

500 to 800 psi. The level of the trifunctional polymer TP4040 is the primary means permitted for controlling this property. The amount of TP4040 required with a given set of raw materials is determined experimentally by preparing and testing a series of small mixes with different TP4040 contents.

The new lot of NPGA and other raw materials associated with it in production required that 2% TP4040 be used in the sustainer propellant, which is the minimum amount permitted by the propellant specification. Even so, the modulus at 25°C was just under the maximum limit, effectively preventing the use of more TP4040 to reduce the insoluble submix fraction in production mixes.

Stress analysis of the Improved HAWK motor showed that the stresses on the bonded interfaces were a function of propellant modulus. Modulus and temperature are inversely related, so the greatest stresses occur at the lowest temperatures. Indeed, motor unbonds were found only after exposure to temperatures below -30°C. Mechanical property data on sustainer propellants removed from dissected motors showed that the new lot of NPGA and its associated raw materials had produced propellant with significantly higher modulus at low temperature than the old lot.

Experimental 6-kg propellant mixes were made with the old and new lots of NPGA at TP4040 levels of 2.0%, 3.5%, and 5.0%. After cure, the propellants were tested for mechanical properties at 25°C and -40°C. Die-cut tensile specimens with a gauge length of 2.70 in. were strained at a rate of 2.0 in./min. The properties are listed in Table 5; the moduli are shown graphically in Figure 5.

The most striking feature of the data is that the -40°C modulus decreased with increasing TP4040 level, while the 25°C modulus increased as expected. Inspection of the -40°C stress-strain curves showed that the curve shape changed with TP4040 content (Figure 6). This effect was attributed to the insoluble submix fraction, with the -40°C modulus responding in a manner somewhat analogous to the viscosity at low shear stress.

Another feature in the data was puzzling on first inspection: the new lot of NPGA, with a lower effective functionality, gave higher 25°C moduli at all TP4040 levels than the old lot. This was explained by the fact that the insoluble fraction was chiefly NPGA and B2000 with functionalities of 1.66 and 2.0, respectively. Removal of these lower functionality materials through immiscibility increased the average functionality of the remainder, thus increasing the 25°C modulus. When the new, less soluble lot of NPGA was introduced, the 25°C modulus

of the propellant increased. In response, the TP4040 level was reduced to stay within the specified modulus range, which in turn further decreased the solubility of the NPGA. Simultaneously, the -40°C modulus increased markedly, placing heavy stresses on the bonded interfaces.

Discussion of the foregoing data with stress analysts led to the conclusion that it would be preferable to accept higher 25°C moduli to reduce the -40°C moduli. Subsequently, the maximum modulus limit at 25°C was raised from 800 to 1000 psi, permitting the use of 4% TP4040. This greatly reduced the -40°C modulus, which increased the bond safety margin calculated from the stress analysis. No unbonded motors have been found among several hundred produced since this change was incorporated.

PROCESS CHANGES TO ACHIEVE SOLUBILITY

Despite the success achieved through raising the TP4040 content by waiving the 25°C modulus requirement, it remained very desirable to eliminate all effects of an immiscible binder component on propellant processing and mechanical properties. Because the motor is in production internationally, major changes to material specifications were not considered as viable options. Only process changes were viewed as acceptable approaches to increasing the solubility of NPGA.

A review of the chemical kinetics of the cure reactions suggested that changing the order of certain reactions might be effective. NPGA has primary hydroxyl groups which are far more reactive toward HDI than the secondary hydroxyl groups of TP4040 and B2000. Therefore, the first principle products of the submix-HDI reaction would be HDI capped NPGA and chain-extended NPGA. Because high-molecular weight NPGA was shown to be the insoluble portion, any chain extension would aggravate the problem. Therefore, mixtures which contain both NPGA and HDI at their maximum concentrations should be avoided.

The approach to minimizing NPGA chain extension was to withhold the NPGA from the mix until a substantial amount of reaction had occurred between HDI and the other polymers. This reduced the amount of difunctional HDI which would be available to chain extend the NPGA, and simultaneously changed the solvent nature of the submix by introducing urethane linkages. Thus the NPGA, when added late, was introduced into a different chemical environment than in the regular procedure.

The technique of late NPGA addition had a pronounced effect on propellant processing and mechanical properties. Propellant viscosity at the end of the mix cycle was drastically reduced and thixotropy

was essentially eliminated. Viscosity data are shown in Table 6 for the same formulation made by the two processes, using the new lot of NPGA. The very low viscosities resulting from late addition of NPGA would be expected to eliminate the possibility of poor wetting by the sustainer propellant, and provide a number of other processing advantages as side benefits.

The effects of late NPGA addition on mechanical properties are shown in Figures 7 through 10 as a function of temperature. Figure 7 shows that late addition greatly reduced the initial modulus of the propellant across the temperature range. The 50% reduction at 25°C was attributed to a reduction in average binder continuum functionality resulting from greater solubility of the NPGA. This reduction in modulus is the desirable direction of change, because it would permit more TP4040 to be used without exceeding the 25°C modulus limit. At -40°C the relative reduction in modulus was even greater than at 25°C. This was interpreted to be a result of a smaller insoluble submix fraction. As previously discussed, low temperature modulus is a determinant of bond stresses; the low value resulting from late addition was decidedly advantageous. Figure 8 shows the effect of late NPGA addition on propellant tensile strength. The reduction in tensile strength was the expected result of the reduced modulus but the values remained well above specification requirements. The response of tensile strength to temperature was not significantly different for the two processing techniques. Figure 9 shows the effect of late addition on the ratio of tensile strength to modulus. In the investigation of motor unbonds this property proved to be an indicator of the tendency of the propellant to debond. It was seen that late NPGA addition markedly increased this ratio over the temperature range of interest. Figure 10 shows the effect of late addition on propellant strain capability. Again, a very large difference was seen for the two processing techniques. A portion of the increase resulting from late NPGA addition is attributed to the reduction in modulus shown in Figure 7. However, the magnitude of the difference was too great to attribute to this one factor. A large part of the increase was thought to be due to improved binder properties resulting from the NPGA being in solution. Late addition of NPGA is being evaluated further in anticipation of incorporating this process change into the production procedures for Improved HAWK motors.

ACKNOWLEDGMENTS

The authors express their appreciation to the Aerojet Solid Propulsion Company for portions of the data and to Dr. James Carver of the Propulsion Directorate for the GPC characterizations.

TABLE 1. SPECIFICATION FOR NPGA AND ANALYTICAL DATA FOR OLD AND NEW LOTS

Characteristic	Specified Limits	Old Lot	New Lot
Water (%)	0.0% maximum	0.028	0.010
Hydroxyl No.	52.5 to 57.5	56.8	51.9
Acid No.	1.5 maximum	0.60	0.19
Tin (ppm)	50 maximum	5	5
Volatiles (%)	0.5 maximum	0.09	0.10
Refractive Index	1.466 to 1.468	1.46670	1.46670
Viscosity, 25°C (cps)	9000 to 14,000	12,100	12,400
Reactivity	800 to 2100	800	1100

TABLE 2. NPGA CHARACTERISTICS NOT INCLUDED IN SPECIFICATION REQUIREMENTS

	Old NPGA	New NPGA
Number (average molecular weight)	1904	2080
Weight (average molecular weight)	3169	3910
Polydispersity	1.77	1.88
Effective Functionality	1.72	1.66
Viscosity at 25°C	2.80	2.84
Viscosity at 45°C		

TABLE 3. GPC DATA FOR THE INSOLUBLE SUBMIX FRACTION AND FOR NEAT NPGA (NEW LOT OF NPGA, 6% TP4040 IN SUBMIX)

	Insoluble Fraction	Neat NPGA
Number (average molecular weight)	3556	2080
Weight (average molecular weight)	6643	3910
Polydispersity	1.87	1.88

TABLE 4. COMPOSITION OF THE INSOLUBLE SUBMIX FRACTIONS (2% TP4040 IN SUBMIX)

	Old NPGA	New NPGA
NPGA (%)	67	69
Isodecyl pelargonate (%)	16	15
TP4040 (%)	5	2
B2000 (%)	12	14
Weight (average molecular weight)	4605	4581
Hydroxyl No.	30.4	32.4
Submix hydroxyl No.	39.0	39.9

TABLE 5. MECHANICAL PROPERTIES OF SUSTAINER PROPELLANT AT VARIOUS TP4040 LEVELS

Temperature	TP4040 (%)	Property	Old Lot	New Lot
25°C	2.0	Stress (psi)	142	118
		Strain (%)	66.1	63.2
		Modulus (psi)	680	800
25°C	3.5	Stress (psi)	154	138
		Strain (%)	62.7	58.9
		Modulus (psi)	820	910
25°C	5.0	Stress (psi)	167	162
		Strain (%)	56.6	52.6
		Modulus (psi)	940	1060
-40°C	2.0	Stress (psi)	360	340
		Strain (%)	78.3	75.4
		Modulus (psi)	3560	5600
-40°C	3.5	Stress (psi)	415	391
		Strain (%)	74.8	75.8
		Modulus (psi)	2890	3920
-40°C	5.0	Stress (psi)	450	452
		Strain (%)	71.6	62.1
		Modulus (psi)	2510	2840

TABLE 6. VISCOSITY DATA FOR PROPELLANT MIXES MADE WITH REGULAR AND LATE ADDITION OF NPGA*

Shear Stress	Viscosity (kilopoise)	
	Regular Process	Late Addition of NPGA
5000 dynes/cm ²	22	1.0
Infinite	4.8	0.6

*New lot of NPGA

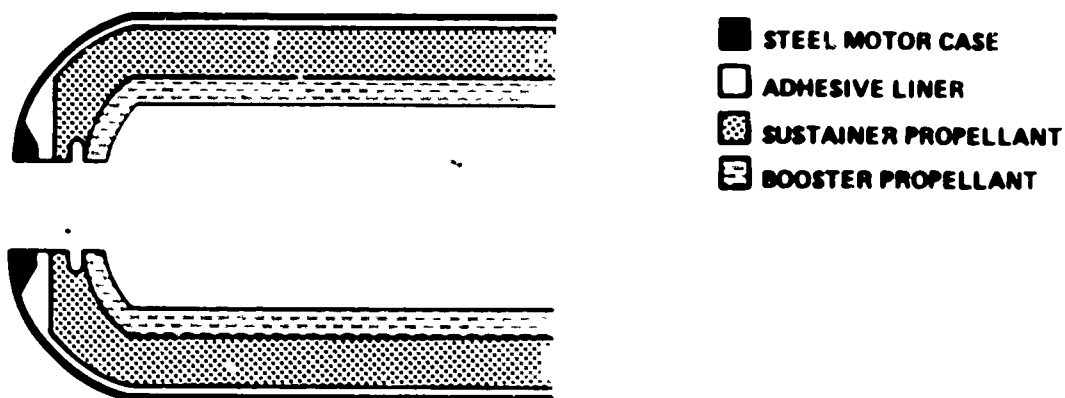


Figure 1. Schematic drawing of the forward end of the Improved HAWK rocket motor.

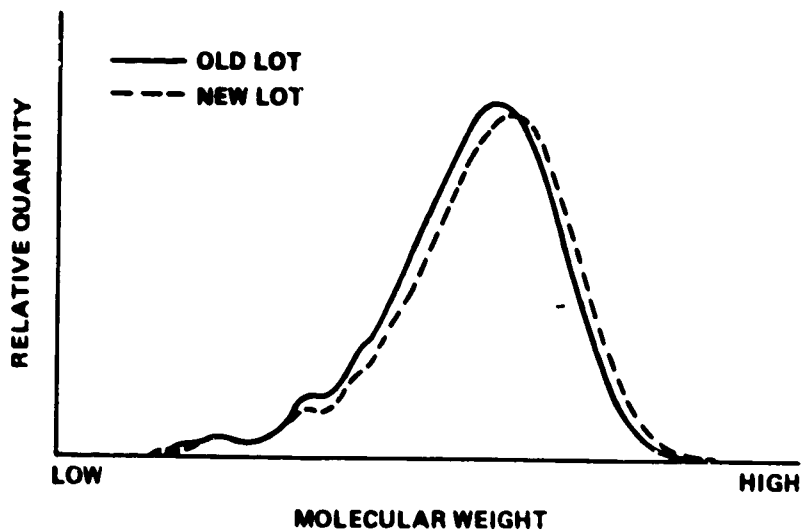


Figure 2. GPC analysis of old and new lots of NPGA.

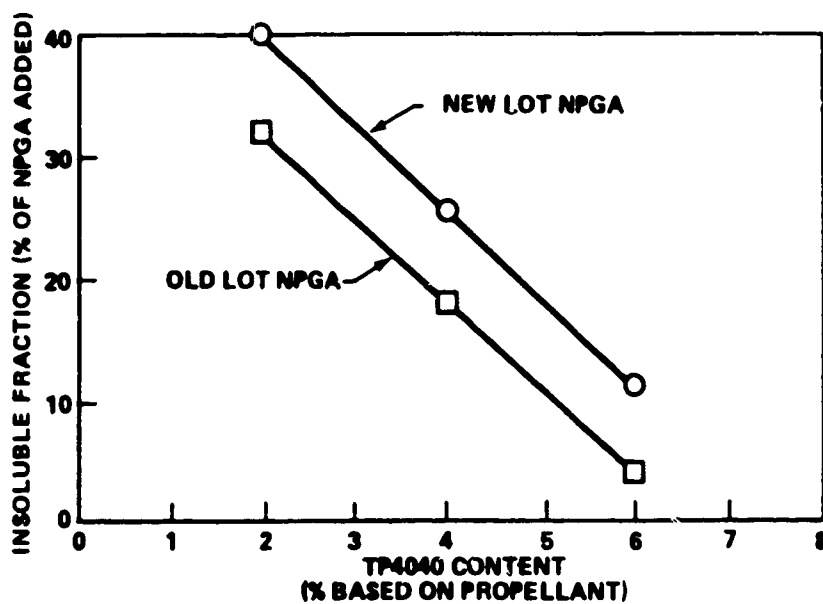


Figure 3. Insoluble fraction of submix versus TP4040 content of submix, for old and new lots of NPGA.

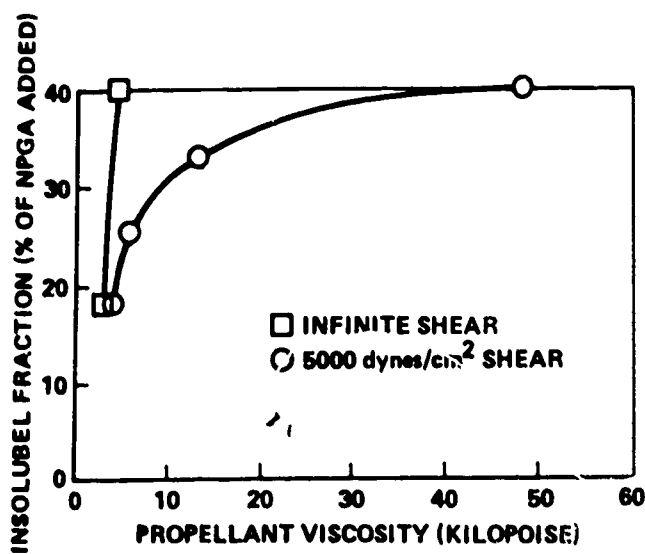


Figure 4. Effect of the quantity of insoluble fraction on propellant processing viscosity (new lot of NPGA)

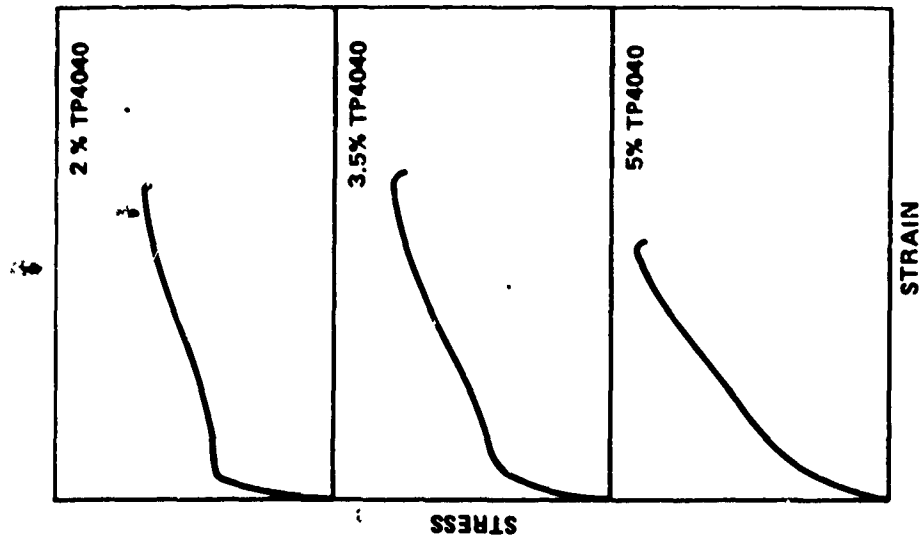


Figure 6. Effect of TP4040 content on the stress-strain behavior of sustainer propellant at -40°C.

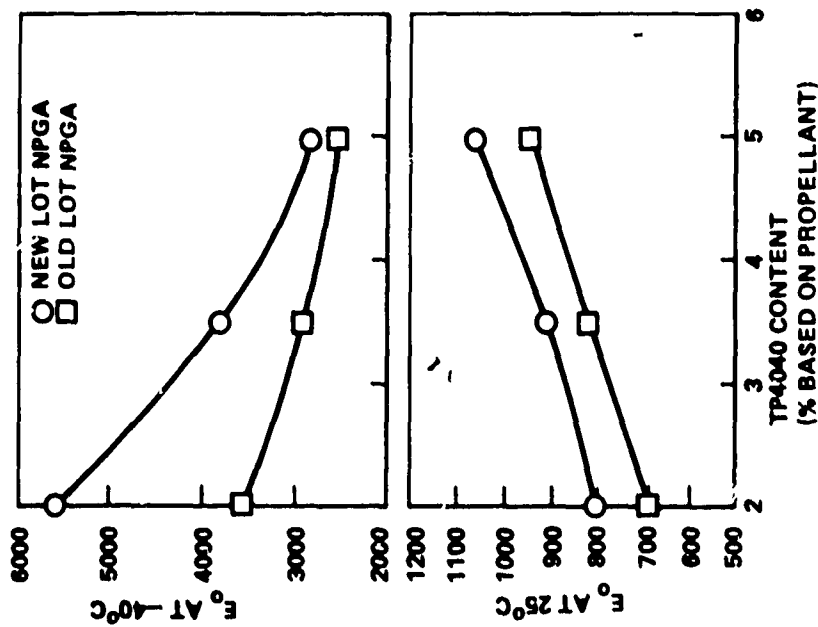


Figure 5. Effect of TP4040 content on the modulus of sustainer propellant at 25°C and -40°C.

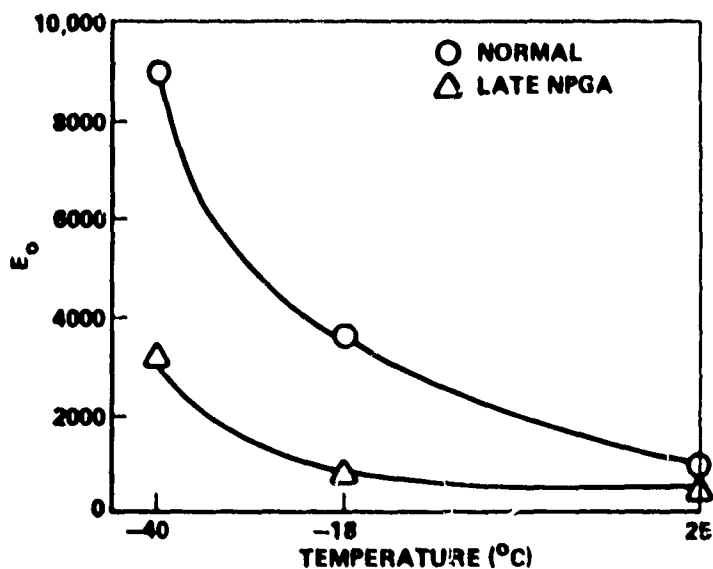


Figure 7. Effect of late NPGA addition on initial modulus.

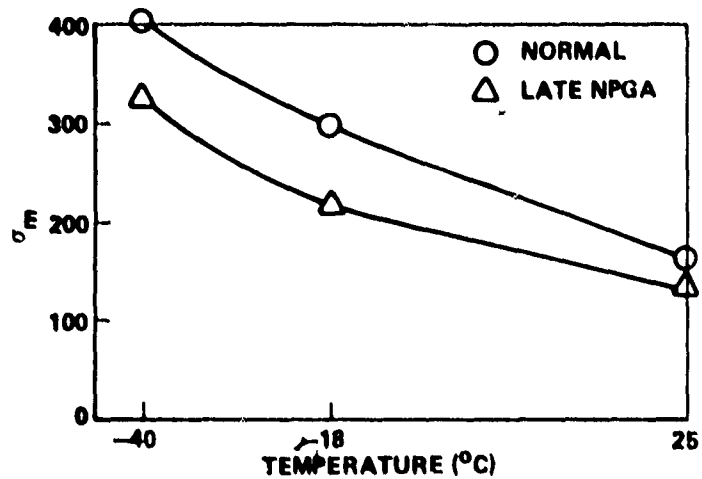


Figure 8. Effect of late NPGA addition on tensile strength.

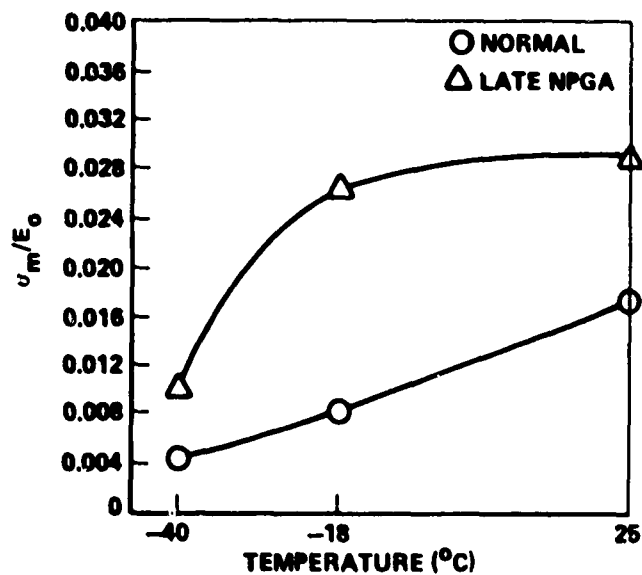


Figure 9. Effect of late NPGA addition on stress/modulus ratio.

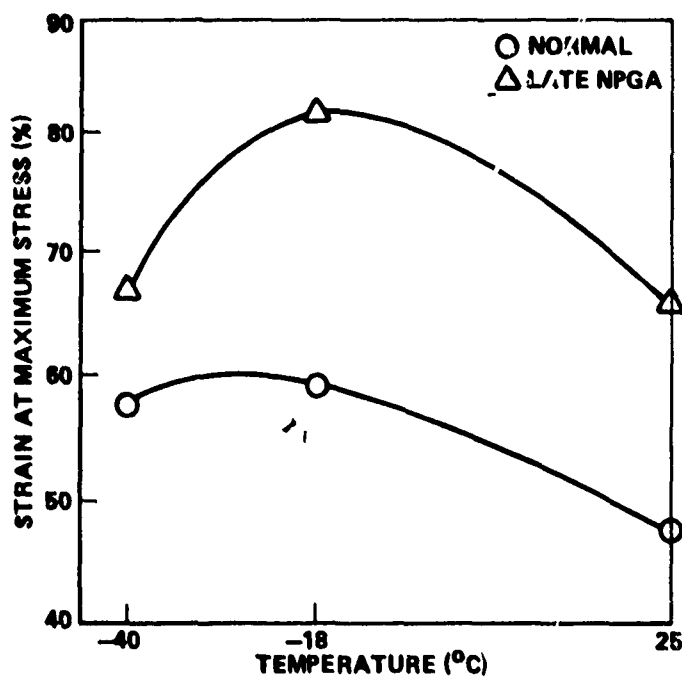


Figure 10. Effect of late NPGA addition on strain capability.